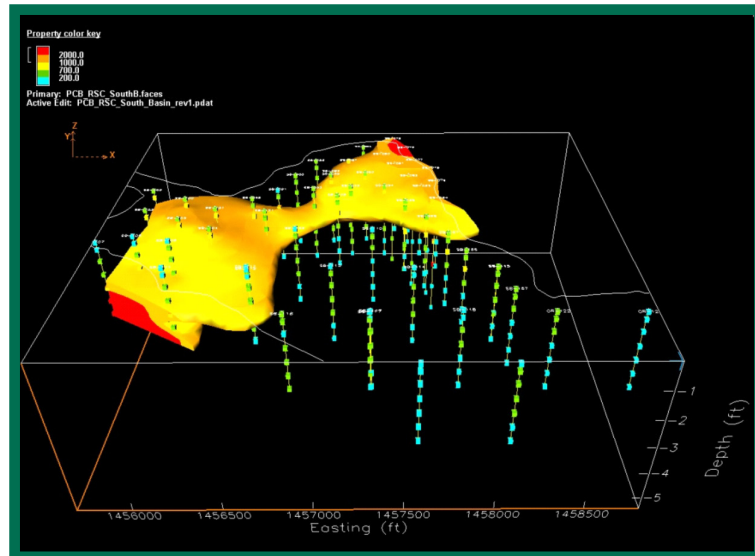


ESTCP Cost and Performance Report

(ER-200826)



Integrated Forensics Approach to Fingerprint PCB Sources using Rapid Sediment Characterization (RSC) and Advanced Chemical Fingerprinting (ACF)

October 2012



ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE OCT 2012		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Integrated Forensics Approach to Fingerprint PCB Sources using Rapid Sediment Characterization (RSC) and Advanced Chemical Fingerprinting (ACF)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program (ESTCP)				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 45	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

COST & PERFORMANCE REPORT

Project: ER-200826

TABLE OF CONTENTS

	Page
1.0 EXECUTIVE SUMMARY	1
1.1 OBJECTIVES OF THE DEMONSTRATION.....	1
1.2 TECHNOLOGY DESCRIPTION	1
1.3 DEMONSTRATION RESULTS.....	1
1.4 IMPLEMENTATION ISSUES	2
2.0 INTRODUCTION	3
2.1 BACKGROUND	3
2.2 OBJECTIVE OF THE DEMONSTRATION.....	6
2.3 REGULATORY DRIVERS	6
3.0 TECHNOLOGY	7
3.1 TECHNOLOGY DESCRIPTION	7
3.2 ADVANTAGES AND LIMITATION OF THE TECHNOLOGY	9
4.0 PERFORMANCE OBJECTIVES	11
4.1 PERFORMANCE OBJECTIVE 1: RSC/ACF PARCC PARAMETERS.....	11
4.1.1 Success/Failure	11
4.2 PERFORMANCE OBJECTIVE 2: DATA ANALYSIS PRECISION AND ACCURACY.....	11
4.2.1 Success/Failure	12
4.3 PERFORMANCE OBJECTIVE 3: QUALITATIVE EASE OF USE	12
5.0 SITE DESCRIPTION	13
6.0 TEST DESIGN	15
6.1 STEP 1: SITE SELECTION FOR FORENSIC STUDY	15
6.2 STEP 2: DEVELOPMENT OF A CSM	15
6.3 STEP 3: DEVELOP AND IMPLEMENT A SAMPLING PLAN	15
6.4 STEP 4: RAPID SEDIMENT CHARACTERIZATION (RSC)	17
6.5 STEP 5: ADVANCED CHEMICAL FINGERPRINTING (ACF)	20
6.6 STEP 6: DATA INTERPRETATION AND REPORTING.....	20
6.6.1 HPS Case Study	21
6.6.2 Ashtabula Case Study	21
6.6.3 Source Confirmation.....	24
7.0 PERFORMANCE ASSESSMENT	25
7.1 PERFORMANCE OBJECTIVE 1: PARCC PARAMETERS FOR RSC/ACF.....	25
7.1.1 RSC Quality Control Results	25
7.1.2 ACF Quality Control Results.....	25

TABLE OF CONTENTS (continued)

	Page
7.2 PERFORMANCE OBJECTIVE 2: DATA ANALYSIS TECHNIQUES	25
8.0 COST ASSESSMENT.....	29
8.1 COST ANALYSIS.....	29
9.0 IMPLEMENTATION ISSUES	31
10.0 REFERENCES	33
APPENDIX A POINTS OF CONTACT.....	A-1

LIST OF FIGURES

	Page
Figure 1.	HPS location map showing South Basin area where cores for this study are located. 4
Figure 2.	Ashtabula River Dredge site with highlighted United States Environmental Protection Agency (EPA) Office of Research and Development (ORD) study area where cores used in this study originate. 5
Figure 3.	Sampling design map for the HPS feasibility study (Battelle, 2007). 16
Figure 4.	Sampling design map for Ashtabula River transect cores (Battelle, 2010). 16
Figure 5.	Example RSC 3D contour maps from HPS (micrograms per kilogram [µg/kg] or ppb total PCB). 18
Figure 6.	Example Ashtabula 3D contour maps (µg/kg or ppb total PCB). 19
Figure 7.	HPS EM source compositions and EM percent in selected cores. 22
Figure 8.	Ashtabula EM compositions. 23
Figure 9.	Selected Ashtabula cores showing EM percent compositions and total PCB levels (ppm). 23
Figure 10.	Comparison of source compositions derived from ALS (row 2), PMF (row 3), PVA (row 4), and Unmix (row 5). 26
Figure 11.	Comparison of source apportionment derived from PMF, PVA, Unmix, and ALS for surface sediments. 27

LIST OF TABLES

	Page
Table 1.	
Performance objectives.....	11
Table 2.	
Approximate costs for a contaminated sediment forensics study.....	30

ACRONYMS AND ABBREVIATIONS

µg/kg	micrograms per kilogram
3D	three-dimensional
ACF	Advanced Chemical Fingerprinting
ALS	alternating least squares
COPC	contaminants of potential concern
CSM	conceptual site model
CSO	combined sewer outfall
DEM	demonstration
DoD	Department of Defense
DQO	data quality objective
ECD	electron-capture dissociation
EM	end-member
EPA	United States Environmental Protection Agency
ER	Environmental Restoration
ESTCP	Environmental Security Technology Certification Program
FS	Feasibility Study
G	factor score matrix
GC	gas chromatography
HCA	hierarchical cluster analysis
HPS	Hunters Point Shipyard
HRGC	high-resolution gas chromatography
HRMS	high-resolution mass spectrometry
LRMS	low-resolution mass spectrometry
MS	mass spectrometry
mg/kg	milligrams per kilogram
NOAA	National Oceanographic and Atmospheric Administration
ORD	Office of Research and Development
PAH	polycyclic aromatic hydrocarbon
PARCC	precision, accuracy, representativeness, completeness, and comparability
PCA	principal component analysis
PCB	polychlorinated biphenyl
PMF	positive matrix factorization
ppm	parts per million

ACRONYMS AND ABBREVIATIONS (continued)

ppb	parts per billion
PRP	potentially responsible party
PVA	polytopic vector analysis
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RI	Remedial Investigation
RPM	Remedial Project Manager
RSC	rapid sediment characterization
SIM	selected ion monitoring
SMCR	self-modeling curve resolution
SPAWAR	Space and Naval Warfare Systems Command
TMDL	total maximum daily load
VAL	validation

ACKNOWLEDGEMENTS

The project team gratefully acknowledges the financial and technical support provided for this project by the Environmental Security Technology Certification Program (ESTCP). We thank Dr. Andrea Leeson and Dr. Jeff Marqusee from ESTCP for their guidance.

*Technical material contained in this report has been approved for public release.
Mention of trade names or commercial products in this report is for informational purposes only;
no endorsement or recommendation is implied.*

This page left blank intentionally.

1.0 EXECUTIVE SUMMARY

1.1 OBJECTIVES OF THE DEMONSTRATION

This Cost & Performance Report was prepared for Environmental Security Technology Certification Program (ESTCP) Environmental Restoration (ER) Project ER-200826 “Integrated Forensics Approach to Fingerprint Polychlorinated Biphenyl (PCB) Sources using Rapid Sediment Characterization (RSC) and Advanced Chemical Fingerprinting (ACF).” We demonstrate an integrated approach to fingerprint sediment PCB contamination that combines sediment screening technologies on a large number of field samples followed by detailed PCB congener analysis in conjunction with ACF interpretation on a subset of selected laboratory samples to identify PCB sources to sediments. The current alternative approach without a forensics study merely assumes the most visible landholder (often a Department of Defense [DoD] facility) closest to the sediment contamination is responsible. The performance assessment shows the PCB analytical measurements meet the required data quality objectives (DQO) and the investigation techniques show reproducible results with simple artificial datasets as well as the real demonstration site datasets. Investigation techniques (including receptor models) were successful in reproducing original source signatures from artificial datasets that were constructed by mixing the original sources in varying proportions. Additionally, a real dataset from a demonstration site was used to show different investigation techniques produce comparable source results.

1.2 TECHNOLOGY DESCRIPTION

The demonstration includes these two technology components: 1) RSC technologies that provide for wide spatial and temporal coverage to delineate sediment contaminant gradients and semi-quantitative characterization in a cost-effective manner; and 2) ACF on a selected subset of samples to delineate sources. ACF includes both advanced laboratory chemical analysis of samples, and the application of sophisticated data analysis and interpretation methods. The combined use of RSC and ACF, however, are only two steps in the overall Integrated Forensics Approach that is modified from our earlier fingerprinting work (Stout et al., 2003). The overall sequence of steps, or tasks, that will be employed include 1) evaluation of the site’s potential as a demonstration site, 2) development of a conceptual site model (CSM), 3) development and implementation of a defensible study design, 4) demonstration of RSC screening, 5) demonstration of ACF, and, finally, 6) synthesis and presentation of the results in a final report.

1.3 DEMONSTRATION RESULTS

The forensic study results from the two demonstration sites indicate both sites have multiple PCB sources to the sediments that were successfully discriminated by the demonstrated Integrated Forensics Approach. At Hunters Point Shipyard (HPS), there are three source patterns that appear to originate from two different areas. In the more recent surface sediment on the east side of the embayment near the former landfill, an Aroclor 1260 pattern is clearly seen which appears to originate from the upland landfill area. In the more recent surface sediments on the west side of the embayment near Yosemite Creek, a mix of Aroclors 1260/1254/1248 is present and appears to be from combined sewer outfalls (CSO). A third pattern appears more common in

the deeper sediments (prior to 1970 when the highest PCB concentrations are present) from both sides of the embayment that is approximately a 50% mix of Aroclors 1260/1254. At Ashtabula River, there are four PCB compositional patterns that appear to originate from two different areas. Most of the sediments in the dredge area contain an Aroclor 1248 pattern, some of which show varying amounts of a second dechlorination pattern. These two patterns probably represent the same source of PCBs and are reported to be from Fields Brook. A third, deeper sediment pattern also believed to be from Fields Brook is seen in most cores (in sediments deposited prior to last dredge event in the early 1960s) with a unique pattern enriched in highly chlorinated PCB congeners (e.g., PCB209). A fourth, very recent pattern contributing Aroclor 1260 is observed in surface sediments and has been traced back to a drainage creek discharging from the west side of the Ashtabula River opposite from Fields Brook. When PCB mass is considered in addition to just PCB proportions, the Ashtabula dredge area shows greater than 99% of the PCB mass with compositional patterns that can be traced back to sources in Fields Brook. The similarity in the three source patterns from HPS makes the apportionment less certain at that site compared to the four source patterns at Ashtabula which show more unique characteristics that allow more precise apportionment.

1.4 IMPLEMENTATION ISSUES

As discussed in several sections of this report, the most important aspects to conducting a successful forensics study are to have high quality PCB data and experienced analysts interpreting the results. It is also important to have a technically defensible approach (such as the one described in this report) so that the DoD's fingerprinting case is fairly represented. It does not appear to matter which particular investigation technique (specific receptor model) is used, and in fact a weight of evidence approach which looks at a number of independent lines of evidence is probably best. Also important is to present the information in a number of ways to ensure it is communicated to an audience with varying levels of forensic expertise (such as receptor model details presented to forensic experts, and spatial displays such as contour maps of PCB concentrations or source proportions presented to the general public). All of the techniques discussed in this report are commercially available from multiple sources. The analytical techniques are available from contractors that can provide high quality data. The number of individual PCB congeners that can be expected to be above detection limits will be related to the total concentration of the samples, and samples with total PCB concentrations below about 100 parts per billion (ppb) will typically not have enough congeners above detection limits to be useful for forensic study. The data analysis and interpretation techniques are also widely available from multiple contractors. These contractors should also have experience with many types of visual displays that can be used to present the data in the best, most comprehensible fashion. Additional guidance on conducting a fingerprinting study can be found in a companion user's guide on the Navy's Space and Naval Warfare Systems Command (SPAWAR) website (http://environ.spawar.navy.mil/Projects/PCB_Fingerprinting).

2.0 INTRODUCTION

This Cost & Performance Report was prepared for ESTCP Project ER-200826 “Integrated Forensics Approach to Fingerprint PCB Sources using RSC and ACF.” Dr J.M. Leather, who is the principal investigator of the project, received demonstration (DEM)/validation (VAL) funding under ESTCP. This project demonstrated and validated an innovative and powerful procedure to fingerprint the sources of PCBs to sediments. The technology includes two primary components: 1) RSC (such as immunoassays for total PCB analysis) technologies that provide for wide spatial and temporal coverage to delineate sediment contaminant concentration gradients in a cost effective manner; and 2) ACF on a selected subset of samples to delineate sources. ACF includes both advanced laboratory chemical analysis of samples (such as laboratory congener analysis), and the application of sophisticated data analysis and interpretation methods.

This project conducted two demonstrations on previously collected data from two different types of regulatory projects. The first demonstration site was in the South Basin at HPS, located just south of San Francisco, CA (Figure 1). This site had an extensive PCB dataset that was available from the regulatory Remedial Investigation (RI)/Feasibility Study (FS) recently conducted at the site (Battelle, 2007). It represents a typical DoD sediment cleanup site with a former landfill and nearby creek with CSOs that represent multiple potential PCB sources. Total PCB concentrations in the sediments are up to 20 parts per million (ppm) in a relatively quiescent estuarine depositional setting. The second demonstration site was at the Ashtabula River Dredge site, located just east of Cleveland, OH (Figure 2). This site represents a typical dredge site, where multiple potential upstream sources contribute total PCB concentrations in the downstream sediments up to 200 ppm (Battelle, 2010). It is a more dynamic fresh water site which shows that PCBs in industrial settings can move from distant source areas and be present in dredged sediments where ownership needs to be apportioned. This second demonstration site was also selected to highlight some alteration issues that we were not able to show at our first demonstration site. Due to the large amount of pre-existing data that were available to leverage into this project, no additional fieldwork was conducted for this project. This provided a great amount of cost savings for the project and reduced the size and complexity of this ESTCP demonstration.

2.1 BACKGROUND

Sediments are often considered the ultimate sink for contaminants in aquatic settings. Once in the sediments, however, contaminants may be reintroduced into the overlying water column or the biological community by a number of physical, chemical, and/or biological processes. Determining the original source of contamination to a heterogeneous matrix such as sediments is a requirement for both Clean-up and Compliance programs within the military. In recognition of this requirement, the approach more fully described in Section 5 includes the combined use of rapid field analytical technologies to map sediment contaminant plumes and ACF on a subset of samples to identify sources. This provides a cost-effective and technically advanced and defensible approach to characterizing the PCB contamination and its sources. The current alternative approach without a forensics study merely assumes the most visible landholder (often a DoD facility) closest to the sediment contamination is responsible.

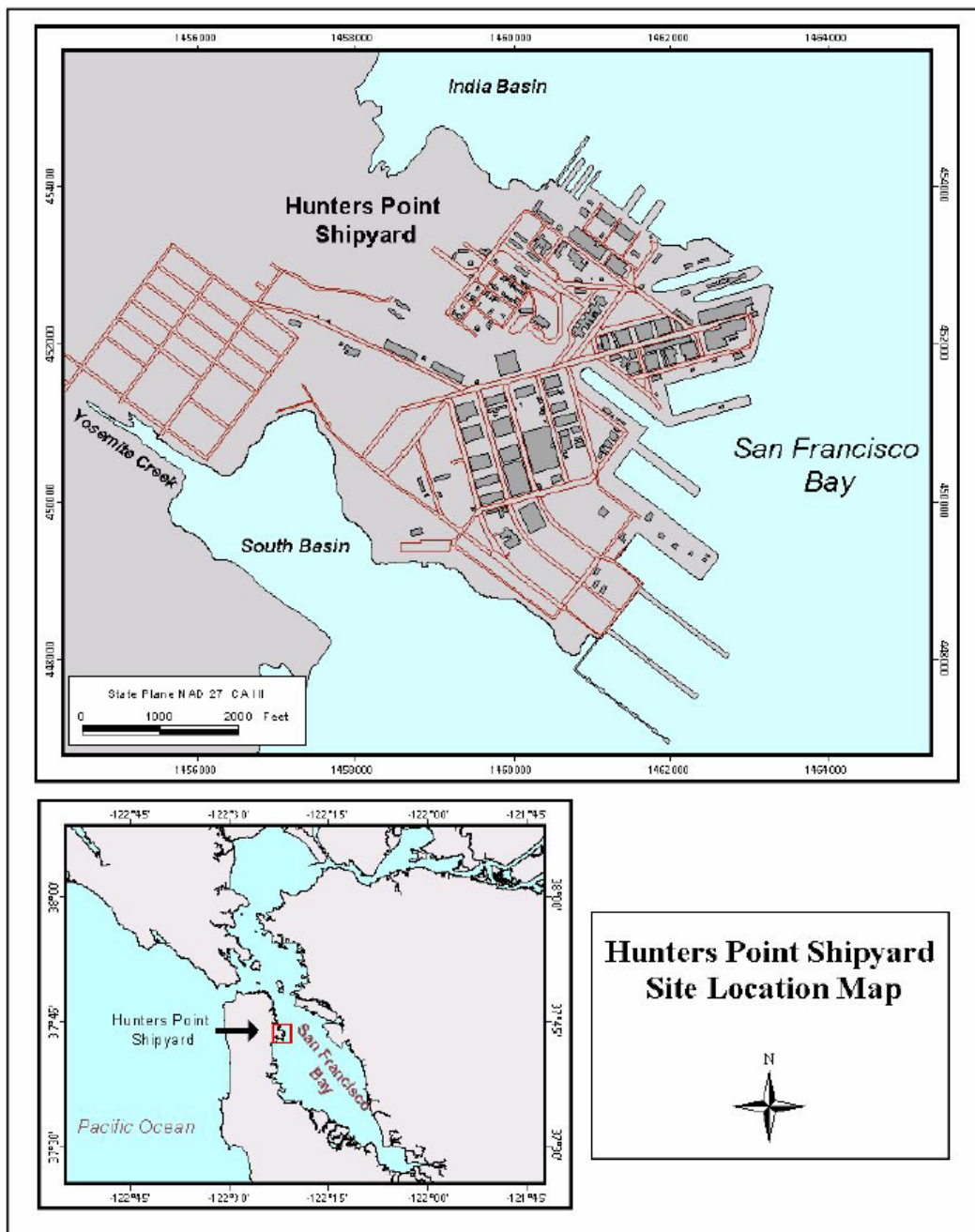


Figure 1. HPS location map showing South Basin area where cores for this study are located.

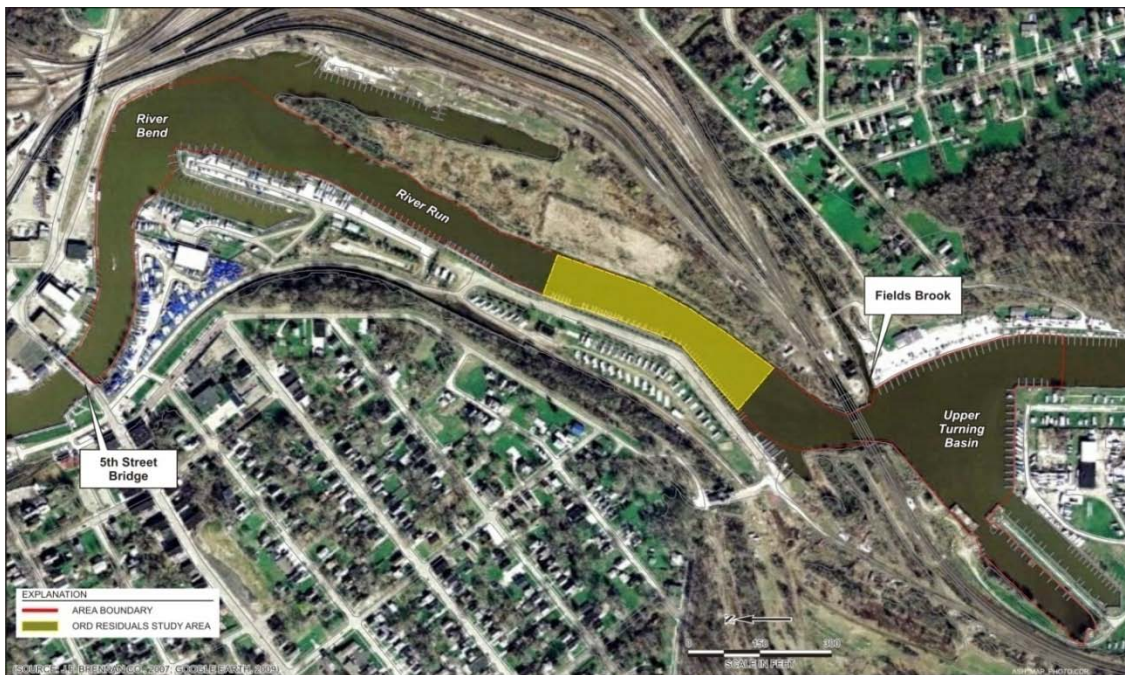
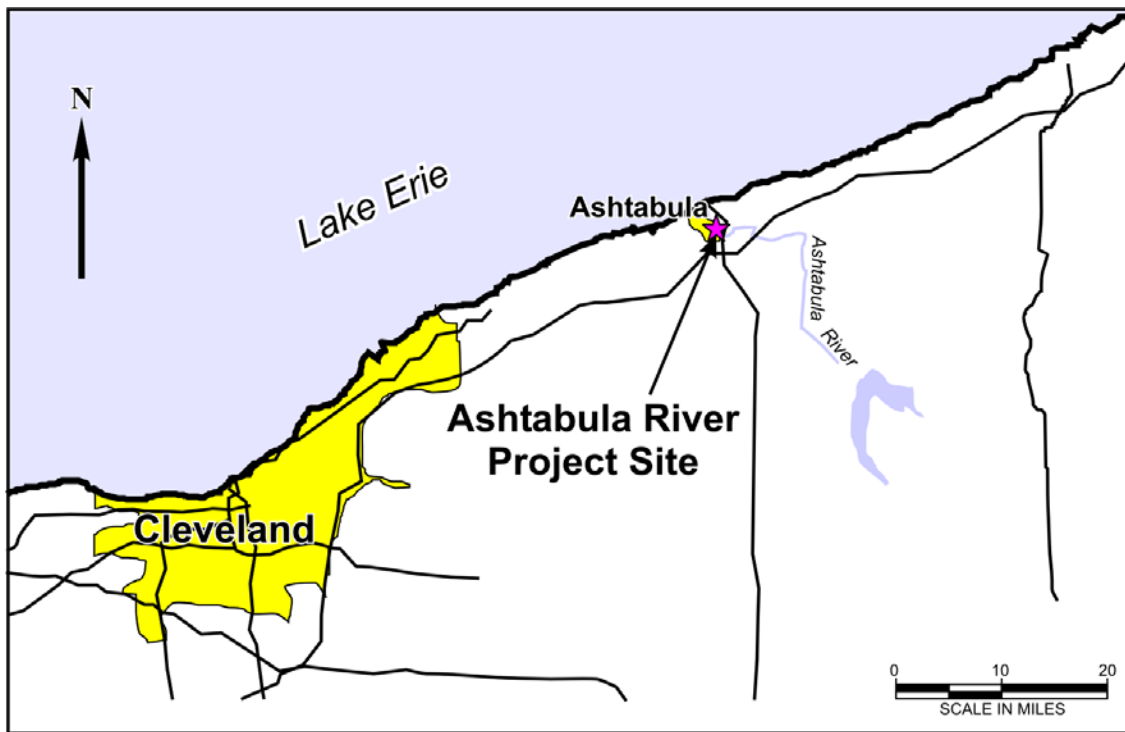


Figure 2. Ashtabula River Dredge site with highlighted United States Environmental Protection Agency (EPA) Office of Research and Development (ORD) study area where cores used in this study originate.
 (note aerial photo is rotated so north is to the left)

The objective of combining RSC with ACF in an Integrated Forensics Approach is to cost-effectively maximize the benefits of each method and to help offset the limitations of each method. This methodology uses a larger number of relatively low cost RSC analyses to map contaminant gradients followed by a subset of samples for ACF analyses with advanced statistical analyses to actually differentiate source compositions and their relative contributions to the impacted sediments.

2.2 OBJECTIVE OF THE DEMONSTRATION

We demonstrate an integrated approach to fingerprint sediment PCB contamination that combines sediment screening technologies on a large number of field samples followed by detailed PCB congener analysis in conjunction with ACF data interpretation on a subset of selected laboratory samples to identify sources. The combined use of RSC and ACF, however, are only two steps in the overall Integrated Forensics Approach that is modified from our earlier work for polycyclic aromatic hydrocarbon (PAH) fingerprinting (Stout et al., 2003). The overall sequence of steps, or tasks, that will be employed include 1) evaluation of the site's potential as a demonstration site, 2) development of a CSM, 3) development and implementation of a defensible study design, 4) demonstration of RSC screening, 5) demonstration of ACF, and, finally, 6) synthesis and presentation of the results in a final report. This six-step process is developed more fully in Section 5 where it is applied at both the demonstration sites. That section contains a general overview of the above six steps and how they are applied at each of the demonstration sites. In Section 6 we show how all the performance objectives outlined in Section 3 were successfully met.

2.3 REGULATORY DRIVERS

Understanding the source(s) of contaminants to sediment in industrial settings is a prerequisite to implementing any proposed sediment remedial options under Clean-up programs (EPA, 2002). This is due to the fact that the sources must be controlled prior to remedial efforts to ensure that recontamination can be avoided. An additional reason for source identification includes ensuring that costs of any dredging or other remedial efforts can be fairly allocated among multiple potentially responsible parties (PRP). In some instances, elevated levels of PCBs in sediment have led to impairment designations requiring the development of total maximum daily loads (TMDL) and subsequent waste load allocations under state and federal Compliance programs. As a result, development of site-specific forensic investigations and TMDLs are closely linked. The need to develop these types of TMDLs also requires the development and use of a forensics approach to fingerprint contaminant sources so that loads can be allocated.

3.0 TECHNOLOGY

Unraveling the complexity of comingled or overlapping sources of PCB contamination in sediments requires good spatial (and perhaps temporal) coverage of the impacted sediments and a precise chemical characterization of the congener composition of the impacted sediments. These two requirements can be cost-effectively achieved through the combination of the following:

1. RSC of a large number of sediment samples to identify contaminant trends, “hotspots,” and key samples using fast, semi-quantitative, and typically field-deployed methods;
2. ACF of a selected subset of sediment samples to recognize and unravel distinct source “fingerprints” using more advanced laboratory and data analysis methods.

The objective of combining RSC with ACF is to cost-effectively maximize the benefits of each method and to help offset the limitations of each method. For example, RSC provides a cost-effective technique for spatial (and perhaps temporal with core data) coverage, allowing chemical gradients to be determined for initial indications of potential sources. However, it only provides total PCB values and does not allow individual congeners to be determined that may be required for actually fingerprinting sources. ACF normally requires specialty analyses beyond the scope of normal regulatory requirements which require the services of high quality commercial laboratories. In the case of PCBs, many regulatory programs only require the concentrations for total PCBs as Aroclors or maybe the 18 major PCB congeners from the National Oceanographic and Atmospheric Administration (NOAA) Status and Trend Program be determined and reported. However, ACF of PCBs often requires that approximately 50-100 PCB congeners be determined at a higher analytical cost to be able to reliably interpret the data.

3.1 TECHNOLOGY DESCRIPTION

The technology in the Integrated Forensics Approach includes two parts, sediment screening technology to map PCB contamination and ACF to identify PCB sources. These are combined into a forensics approach to cost effectively differentiate and identify multiple sources in an industrial setting. Both analytical chemistry components are modified from standard United States Environmental Protection Agency (EPA) methods, but their integration and use together with innovative data analysis methods in a forensics study are novel and need demonstration and validation using case studies to promote future use.

RSC – RSC of semi-volatile organics can be conducted using commercially available immunoassay test kits as well as other methods (<http://web.ead.anl.gov/ecorisk/issue/pdf/rsc.pdf>). The techniques for the RSC of PCB in sediments have been adapted from methods developed for use in soils. The modifications include dewatering of the sediment and extending the calibration range to reach lower detection limits than standard soil applications. Sample preparation for RSC can be more or less involved depending on the objectives of the project, and may even approach those for standard laboratory methods. For many applications, however, the more basic preparation methods will still meet the project needs and are usually selected so this initial step in the procedure can be conducted in a cost-effective and timely manner. The dewatered sediment is extracted using an organic solvent

(e.g., methanol) and analysis of the extract is then conducted by immunoassay techniques. In the case of the more quantitative immunoassays, the extract is treated with specific antibodies that promote a color change depending upon PCB concentration, which is measured against PCB standards with a solution-calibrated spectrophotometer. All of these procedures are modifications of the current standard immunoassay methods described under EPA Method 4020 (Screening for PCBs by immunoassay) that have been developed at SPAWAR to work on the wet, organic-rich matrix found in many sediments. Although soil detection limits are often quoted to be 500 ppb, these limits can be pushed down to 50-100 ppb when limited site specific matrix interferences are present.

Since every site is different, the manner in which RSC is used to select the ACF samples will be site specific and details may change depending on the site objectives. At our first demonstration site at HPS, we have a fairly simple case where there are two source areas (one to the west by the creek and one to the east by the former landfill) that appear to contribute PCBs that were distributed into a depositional embayment. Generally, samples for ACF should be selected to cover the horizontal and vertical areas of interest, as well as to cover the concentration ranges seen in the RSC data. Areas of high concentration are often indicative of potential source areas so they will be likely candidates for selection of ACF samples. Many lower concentration areas will be of interest to show how the potential sources are mixing over a geographic area of interest. At the Ashtabula River dredge site, we have a similar situation where there are two source areas (one to the east by Fields Brook and one to the west on the other side of the river) that appear to contribute PCBs that mix downstream in the dredge footprint area. If this were a DoD dredge site, the RSC data could have been used to select a subset of ACF samples as described above. However, the EPA Office of Research and Development (ORD) researchers chose to measure all samples for ACF since they had other objectives in characterizing the residual material left behind following the dredge operation. An objective of the EPA ORD research team was to evaluate the use of RSC to screen sediment areas for further forensic study. The RSC data were also used to map initial PCB concentrations and allow the laboratory to group samples by concentration to run in particular dilution batches. Additional discussion of how RSC can be used to select ACF samples can be found in Section 5.4.

ACF by Battelle – The ACF techniques available for the assessment of semi-volatile organic contaminants in sediments (e.g., PCBs) are based on sample analysis using high-resolution gas chromatography (GC), usually operated in conjunction with compound-specific detectors (e.g., electron-capture dissociation [ECD] or mass spectrometry [MS]). Some laboratories have in recent years developed state-of-the-art PCB analytical methods using high-resolution (HR) GC/low-resolution (LR) MS operating in selected ion monitoring mode (HRGC/LRM-SIM), that are both highly cost effective *and* provide detailed, high-quality data (Durell and Seavey, 2000). The methods employ components of EPA Method 680 (HRGC/LRMS PCB homologue and total PCB method) and Method 1668a (HRGC/HRMS PCB congener method). The base methods have been modified for the analysis of more than 120 PCB congeners; the congeners typically detected in PCB formulations and environmental samples and a large number of non-standard environmentally important and diagnostic PCB congeners that will permit data analysis for differentiating potential sources. Typically detection limits for individual congeners range from 0.1 to 0.5 ppb when no site-specific matrix interferences are present.

The data analysis for differentiating contaminant composition, and thus potential sources and source differences, can include but might not be limited to the following (see Johnson et al., 2007 for more discussion):

- Chromatographic and bar chart representation (often referred to as bar chart “fingerprints”) of the PCB homologue and/or PCB congener concentrations and composition of a sample, and reference standards (e.g., source material)
- Diagnostic PCB congener ratio and double ratio crossplots, to separate out similarity and dissimilarity in the chemical composition of samples and sources.
- Decreases in relative concentrations of PCB congeners that are particularly susceptible to dechlorination, and increases in concentrations of dechlorination product PCB congeners.
- Hierarchical cluster analysis (HCA) and principal component analysis (PCA) for the classification of samples, and source materials, with similar and dissimilar PCB composition.
- Multivariate receptor models such as polytopic vector analysis (PVA), positive matrix factorization (PMF), extended self-modeling curve resolution (SMCR) (i.e., EPA’s Unmix), and alternating least squares (ALS) for additional analysis of similarity, dissimilarity, and potential source linkages.

As stated above in discussing the RSC analyses, there are many site-specific differences that make it impossible to describe a single method to explore the data to determine PCB sources. No single data interpretation method should be, or will be, used by itself as “the” single forensic determination method. These are examples of several data analysis methods that can be used, and when taken together the “lines of evidence” help classify samples of contaminant similarity and dissimilarity, including association with sources.

Our Integrated Forensics Approach is demonstrated in Section 5, with the discussion of ACF techniques covered in Section 5.5. We start with the simple PCB congener compositional bar charts (“fingerprints”), look at congener cross-plots, and then show the more advanced multivariate techniques, and let the data dictate how to proceed. In addition to the multivariate approaches, one can often gain significant understanding of PCB transformation and source contamination by closely analyzing specific diagnostic PCB congeners, including ratios of concentrations of labile dechlorination and more persistent stable congeners. Along with all of this, it is very important to incorporate and apply knowledge of PCB congener chemistry and environmental processes to the behavior of PCBs; statistical data analyses alone cannot replace a thorough understanding of PCB chemistry and the combined “weight of evidence” approach is needed for successful PCB forensic applications.

3.2 ADVANTAGES AND LIMITATION OF THE TECHNOLOGY

Although fingerprinting of PAHs is more mature (Stout et al., 2003), work on PCB fingerprinting is rapidly developing and the need for reliable PCB fingerprinting is clearly increasing. Some of the diagnostic principles that are used for PAH fingerprinting can be applied to PCB fingerprinting, but PCB mixtures are vastly different from PAH/petroleum mixtures.

PCBs also behave quite differently in the environment and many factors need to be considered in addition to the most common weathering factors; interpretation methods need to be modified and new data interpretation and analysis considerations need to be developed (Johnson et al., 2006). Emerging PCB fingerprinting techniques have successfully been applied at a few sites in the United States (Johnson et al., 2000; Durell et al., 2001; Emsbo-Mattingly and Durell, 2003; Magar et al., 2005; Johnson et al., 2007), but there is a need to more fully develop, demonstrate, and validate the utility of fingerprinting PCB contamination.

A difference between many of these other previous PCB forensics sites and our demonstration sites is a matter of scale. Much of the previous work has focused on regional scale problems and not the finer scale issues seen at individual DoD sites. DoD sites are typically on the size of acres, whereas other previous work has concentrated on much larger scales (hundreds of miles in San Francisco Bay [Johnson et al., 2000] or the Delaware River TMDL [Rodenburg et al., 2010]). Our demonstration sites were selected to represent the scale of typical DoD sites and address the types of questions posed at DoD sites. The fingerprinting used in these other previous studies was able to determine what the sources were (Aroclor 1248 or 1260), but not the actual location of the sources. Determining the “where” as well as the “what” is why we have RSC technologies integrated into our approach, and why we chose to deal with smaller scale or local source concerns. Local sources also have higher concentration gradients (measured in ppm versus ppb levels in surrounding sediments) because the impacted sediments are closer to these local sources and we can generate contour maps with concentration gradients that help indicate where sources are located. But if total PCB concentrations fall below 100 ppb, many individual congener values will fall below typical detection levels for laboratory methods of 1 ppb so the multivariate interpretation techniques will tend to develop more uncertainty in deriving PCB source information. Additional site information (other upland/upstream studies that provide contaminant source information, sediment transport information to suggest how sediments and contaminants are transported around the site, etc.) will also usually be required in addition to RSC and ACF data to help pinpoint the location of sources and additional PRPs. But if the DoD has PCB-impacted sediments and needs information on the PCB sources that have contributed to their sediments, the Integrated Forensics Approach described in this report can provide a technically-defensible technique to identify these potential sources.

4.0 PERFORMANCE OBJECTIVES

Performance objectives are a critical component of the ESTCP DEM/VAL project (see Table 1). They provide the basis for evaluating the performance and reliability of the technology.

Table 1. Performance objectives.

Performance Objective	Data Requirements	Success Criteria
<i>Quantitative</i>		
RSC and ACF EPA PARCC ^a parameters	Standard QA/QC ^b from regulatory project	See individual criteria in the final report
Receptor model precision/accuracy	Artificial datasets with varying errors and outliers	Ability to reproduce original mixtures
<i>Qualitative</i>		
Ease of use	Feedback on use/time	User evaluations

^aprecision, accuracy, representativeness, completeness, and comparability

^bquality assurance/quality control

4.1 PERFORMANCE OBJECTIVE 1: RSC/ACF PARCC PARAMETERS

Both RSC and ACF measurements are modifications of standard EPA methods, and both can be evaluated by similar standard methods often employed by commercial laboratories. These methods include the evaluation of DQOs that can be characterized by five indicators of data quality referred to as the PARCC parameters: precision, accuracy, representativeness, completeness, and comparability.

4.1.1 Success/Failure

Section 6.1.1 in the project's Final Report contains the results of the performance assessment for the RSC data. Data successfully passed quantitative criteria for the measures of precision and accuracy, and successfully passed the more qualitative criteria for the other PARCC parameters. Section 6.1.2 in the Final Report contains the results of the performance assessment for the ACF congener data. Data successfully passed all DQO requirements with tables in Section 6 of the Final Report listing the success rates for the different types of QC samples.

4.2 PERFORMANCE OBJECTIVE 2: DATA ANALYSIS PRECISION AND ACCURACY

Multiple levels of advanced statistical analyses are possible to investigate the forensics data. These various techniques use slightly different methods, but basically all generate a solution whereby multivariate sample profiles can be interpreted to generate an estimate of the original source compositions. The simplest approaches use PCB congener compositional profiles, other diagnostic ratio crossplots, or modified least squares procedures to generate mixing proportions based on an assumed source profile matrix (e.g., chemical mass balance methods – Hopke, et al., 2006). Such methods work best with a limited number of relatively well known sources. In contrast, more involved self-training receptor modeling methods are better suited to those situations where one does not assume the contributing source fingerprints. These more involved methods include PMF, PVA, Unmix, and ALS (see Johnson, et al., 2007, for more detail on

these methods). These methods differ in their mathematical detail, but are similar in that they do not require assumed source profiles.

4.2.1 Success/Failure

Section 6.2.2 in the Final Report contains the performance assessment done for a group of statistical analyses (receptor models) including ALS, PMF, PVA, and Unmix. Using two different artificial datasets, all these techniques were successful in returning the original sources that were mixed in the artificial datasets. These techniques also gave comparable results for the real HPS dataset, where all techniques found the same three end-member (EM) sources and produced comparable apportionment of these sources across the site. Overall these techniques passed all the performance assessment tests that are presented in detail in Section 6 of the Final Report.

4.3 PERFORMANCE OBJECTIVE 3: QUALITATIVE EASE OF USE

A survey of three Remedial Project Managers (RPM) found multiple contractors who were qualified to perform a PCB forensics study in sediments. The most important aspects were finding a high-quality laboratory for PCB analyses and also people experienced with receptor model applications for PCBs in sediments. One interesting suggestion was that we provide a performance evaluation dataset, something RPMs could use to test the contractors abilities. They suggested using one of the included datasets in the Appendix to test if contractors could reproduce these same solutions.

5.0 SITE DESCRIPTION

Demonstration site locations are shown in Figures 1 and 2. All the site description information was provided in the “Site Selection Memo” which was previously submitted to the ESTCP office as part of each Demonstration Plan. Much of that information is provided in the Final Report and is summarized from a greater depth of information available in the original study documents (Battelle, 2007; Battelle, 2010). The main feature that led to the use of both of these sites in this ESTCP project was the availability of previously obtained PCB data. Both sites had measurements for both RSC and ACF already available as part of their original project. At HPS South Basin (Figure 1), over 50 cores with up to 15 horizons resulted in over 400 samples being measured for RSC. Using these RSC data about 100 samples were selected for ACF, with the original intention of completing a forensics study following the overall approach outlined in Section 5 of this report. However, after all samples were collected and analytical measurements completed, the regulatory project decided not to complete the actual forensics study. These samples were therefore available for this ESTCP project and provided a large leveraged effort from the Navy that resulted in large cost savings for the ESTCP project (Battelle, 2007). At the Ashtabula River dredge site (Figure 2), 30 cores with up to 15 horizons provided about 350 samples that were run for both RSC and ACF. The EPA research team decided to run all samples for ACF (rather than the typical 10-25% of the RSC samples) because the objectives of their original study were to understand the origins of the sediment residuals left behind following dredging (Battelle, 2010). PCB contaminant distributions are shown in the contour maps at the end of Section 5.4.

Although the use of pre-existing data from both sites results in a very cost-effective forensics study, there are some limitations. We had to accept the regulatory project study designs with the number and location of samples that they had chosen. As discussed at the end of Section 5.6, this resulted in a lack of upland/upstream data that could be used to validate the actual source locations for the sources that were found to contribute PCBs to the site sediments. For future forensic studies, it should be a consideration to collect upland/upstream samples for possible confirmation of source locations. This might be done most efficiently in an iterative fashion after initially determining sources and then selecting potential upland/upstream samples based on initial study results.

This page left blank intentionally.

6.0 TEST DESIGN

This section of the report provides the detailed description of the experimental design and the testing recommended to conduct an Integrated Forensics Approach. It also addresses the performance objectives described in Section 3 and evaluated in Section 6. As stated in Section 1.2, since an Integrated Forensics Approach consists of more than just RSC and ACF measurements, this section describes in detail the six steps of the forensics procedure outlined in Section 1.2.

6.1 STEP 1: SITE SELECTION FOR FORENSIC STUDY

The specific reason for whether and why a contaminant source (“fingerprinting”) study should be considered at a particular site will undoubtedly vary for each site. At some sites, the need will be obvious (e.g., the site owner is being held responsible for contamination for which they might not be liable), whereas at others, the need will be less obvious (e.g., the site has agreed to clean up to “background” levels which are poorly established; or the site is one of several potential sources in a complex industrial setting).

6.2 STEP 2: DEVELOPMENT OF A CSM

Once a site’s candidacy has been established, a CSM for the ensuing contaminant source study must be developed, or an existing CSM must be modified. In the case of both our demonstration sites, the existing projects already developed a CSM as part of the Quality Assurance Project Plan (QAPP) that served as a good starting point. At the completion of a CSM, it should be possible to: 1) identify (or confirm the identity of) the known or suspected contaminants of potential concern (COPC) for the site, 2) identify all of the known or suspected sources (or PRPs) of the COPCs within the study area, and 3) develop specific objectives (hypotheses or forensic questions) to be evaluated for the proposed demonstration site.

6.3 STEP 3: DEVELOP AND IMPLEMENT A SAMPLING PLAN

The development of a technically-defensible sampling strategy requires a balance between meeting project and data quality objectives within the budget of the project. The design is typically based upon either some sort of a statistical based sampling (e.g., random, systematic, stratified, cluster, etc.) and professional judgment based upon the information assembled in the CSM during Step 2 above. Sampling designs are often site specific and require consideration of many aspects of the study design. These types of considerations are addressed in many outside references (e.g., Gilbert, 1987, and references herein).

For the HPS demonstration, the regulatory project sampling design map shown in Figure 3 (from Battelle, 2007) was reviewed and the data shown on this map meet the needs of the ESTCP forensics demonstration. For the Ashtabula demonstration, the core locations within the dredge footprint are shown in Figure 4 (Battelle, 2010). By using the existing study designs and sample data from both these demonstration sites it was possible to conduct a very cost-effective forensic study.

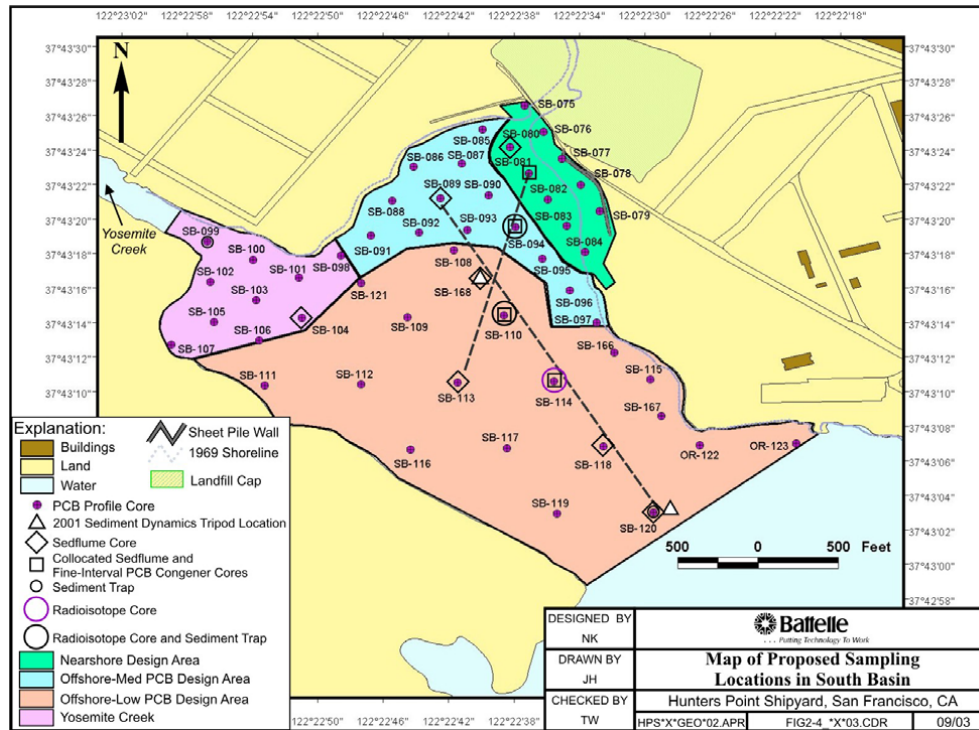


Figure 3. Sampling design map for the HPS feasibility study (Battelle, 2007).
This includes the cores that provided the pre-existing data that was used in the forensics demonstration at HPS.

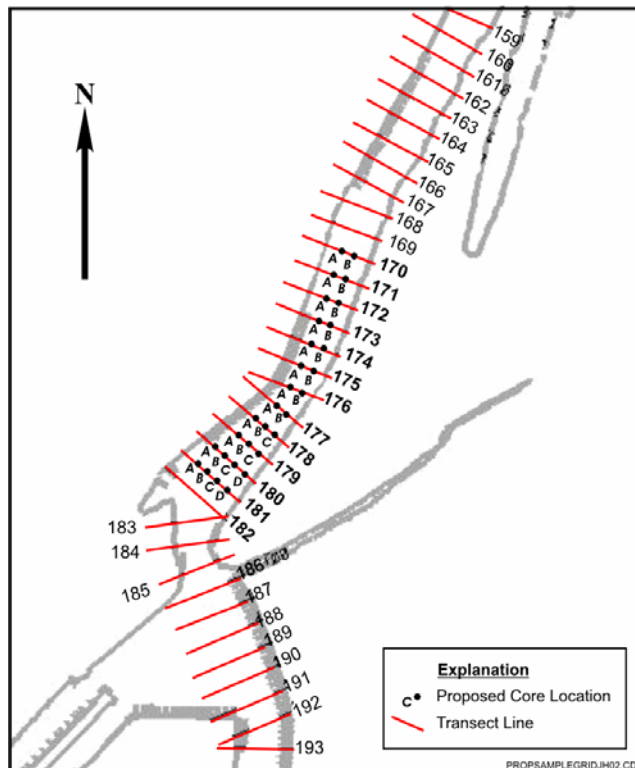


Figure 4. Sampling design map for Ashtabula River transect cores (Battelle, 2010).
These cores provided the pre-existing data used in this forensics demonstration.

6.4 STEP 4: RAPID SEDIMENT CHARACTERIZATION (RSC)

RSC methods have been described in Section 2. Regardless of the approach used in the evaluation of RSC data, it is important to remember that the goal of the RSC data analysis is to develop a sufficient set of site characterization information, including visualizations to aid in the selection of samples for ACF and not to achieve the objectives of the study alone. The analytical strategy and budget will largely determine the number (or percentage) of the RSC samples that will be selected for ACF. Of course, it is not necessary that the entire analytical budget be used if there is no technical basis to do so. For example, if the RSC data have demonstrated uniformity and a predominance of ‘background’ ambient conditions in the study area, the ACF may simply include a few selected confirmation samples. Therefore, the task of selecting samples for ACF is largely a matter of selecting a reasonable and justified subset from the complete set of RSC samples.

Figure 5 shows examples of the contour maps that can be generated with the HPS RSC data to aid in selection of ACF samples. A number of these contour maps can be shown using various PCB concentration levels (e.g., 2,000, 1,000, 700, 200 ppb) to visualize the volumes of sediments that have specific concentrations. The first figure (Figure 5a) shows a three-dimensional (3D) block diagram of the site which has been tilted up at about 45 degrees to show core locations with color-coded sampled horizons which indicate total PCB concentration. This becomes easier to see in Figure 5b where the volume of sediment with PCB concentrations above 2,000 ppb is contoured in red. This visualization makes it easy to see a large mass of PCB contaminated sediment at the mouth of Yosemite Creek (on the west side of the 3D block) and another mass of contaminated sediment along the northeast shoreline of the embayment (near the former landfill).

Figure 6 shows examples of the 3D contour maps that were generated with the core data at the Ashtabula River Dredge site. The first contour map (Figure 6a) shows the core locations with the 1-foot sampled horizons color coded by total PCB concentration levels (red >100,000 ppb, yellow 10,000-100,000 ppb, green 1,000-10,000 ppb, blue 100-1,000 ppb, purple <100 ppb). This figure shows the contoured red outline of the >100,000 ppb sediment volume, with the greater volume of the highest concentrations on the right (south) closer to the upstream sources. The second contour map (Figure 6b) shows all the concentrations contoured to show the 3D aspect of the PCB plume moving downstream to the left (north). Using this contouring procedure, one can map whatever concentration ranges are desired to provide a 3D view of the data. The question to be addressed in this demonstration is whether these contaminated sediments originate from one, two, or more distinct sources. By contouring different PCB levels, the gradients in the concentration data can be visualized and the number and location of samples that will be measured for PCB congener composition can be selected for the next step in the procedure. In the Ashtabula case however, all samples were measured for ACF so we can compare this to the typical procedure of measuring only 10% to 25% of the samples for ACF that was done at our first demonstration site at HPS.

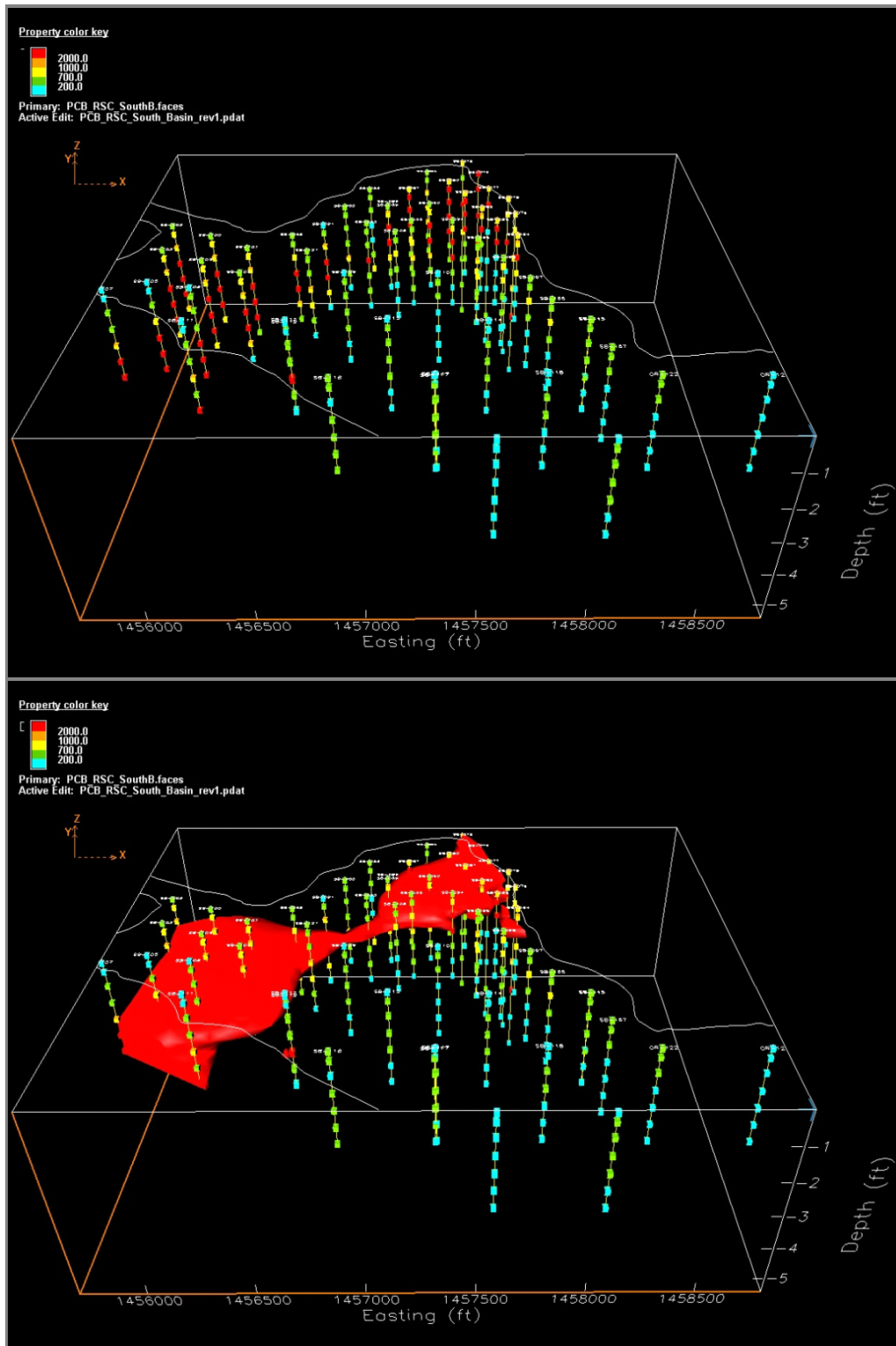


Figure 5. Example RSC 3D contour maps from HPS (micrograms per kilogram [$\mu\text{g/kg}$] or ppb total PCB).

a) color-coded core horizons.

b) >2,000 ppb volume showing two high PCB concentrations areas (from Battelle, 2007).

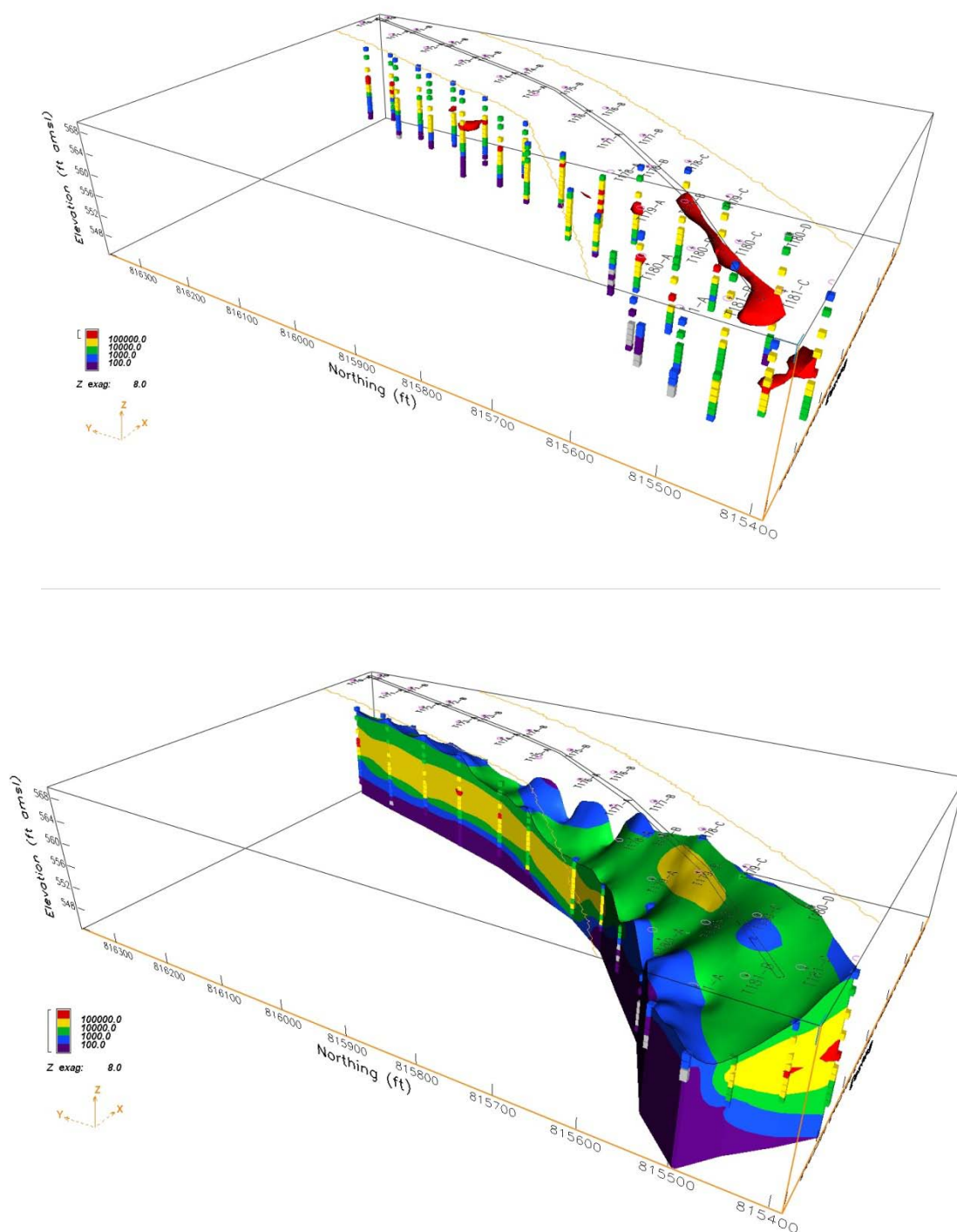


Figure 6. Example Ashtabula 3D contour maps ($\mu\text{g}/\text{kg}$ or ppb total PCB).
 a) $>100,000$ ppb contoured volume.
 b) all contours including >100 , $>1,000$, $>10,000$, $>100,000$ ppb (from Battelle, 2010).

6.5 STEP 5: ADVANCED CHEMICAL FINGERPRINTING (ACF)

The ACF laboratory analytical and interpretation techniques available for the assessment of PCBs in sediments were discussed in detail in Section 2. Once the data are generated they are investigated in a series of ways, generally starting with analytical chromatograms of compositional bar graphs (or bar chart “fingerprints”) to get a preliminary understanding of the PCB composition and compositional variability in the dataset. After comparing these bar chart fingerprints, we often use simple techniques such as congener to congener cross plots to view the compositional variations in the data. It becomes rather tedious to view individual congener cross plots when we have 40 to 100 different congeners, so we need to look at the multivariate techniques that investigate these types of compositional patterns in the entire congener dataset at once. By using multivariate receptor models, we don’t need to assume source compositions, but we can let the receptor models determine what the congener composition of the sources actually are.

The objective of a multivariate approach to chemical fingerprinting is to determine 1) the number of unique source fingerprints present at the site, 2) the chemical composition of each source fingerprint, and 3) the relative contribution of each source fingerprint in each collected sample. Development of numerical methods to determine these parameters has been a major goal in environmental chemometrics and receptor modeling for more than 25 years (Hopke, et al., 2006; Johnson, et al., 2007). Multivariate receptor models have been used increasingly for the characterization of sources and alteration patterns of chlorinated organic compounds in sediments of complex environmental settings (Jarman, et al., 1997; Johnson, et al., 2000; Barabas, et. al., 2004; Imomoglu, et al., 2002; Magar, et al., 2005; Bzdusek, et al., 2006). A review of these methods, with a focus on PCB forensic application, is provided by Johnson et al., 2007. These multivariate receptor models describe the input measurement data as a function of source profiles and source contributions, as shown in the matrix algebra equation $X = GF + E$, where X is the input measurement matrix, G is the source contribution matrix, F is the source profile matrix and E the portion of the measured concentration data that cannot be fit by the model. The basic process involves reducing the original data matrix into a factor loading matrix (F) representing source profiles (shown in Final Report Appendix 1 as EM Compositions) and a factor score matrix (G) representing the source contributions (shown in Final Report Appendix 1 as Mixing Proportions). These various techniques use slightly different methods, but basically all generate a solution whereby multivariate source profiles can be added together according to their source contributions to generate an estimate of each of the original sample compositions.

6.6 STEP 6: DATA INTERPRETATION AND REPORTING

The manner by which the results and conclusions of a contaminant source study are conveyed needs to consider the audience, and particularly their technical experience. The specific target audience will dictate the level of technical detail conveyed in a report or presentation. Chemical “fingerprinting” data in graphical and/or tabulate form can be very confusing to all but an experienced chemist. Their interpretation is much easier (and thereby useful) when the results of a contaminant source study are reported using numerous visual displays that either convey the data spatially or with some other easily interpreted visual. The ideal (but elusive) objective is to present results using data visualization methods that present results accurately and intuitively,

such that both the non-technical manager and the experienced scientist/statistician comprehend the process and understand their results.

6.6.1 HPS Case Study

Figures in this section summarize congener compositional variations along with spatial information to allow us to visualize potential PCB sources in context of the two case studies (HPS and Ashtabula). For example, Figure 7 shows the three proposed HPS EMs (congener compositions determined in Section 5.5 of Final Report) as simple bar chart fingerprints. At the bottom of the figure the spatial distribution of these three fingerprints is shown as a series of down-core plots (see locations from Figure 3). This figure essentially shows a transect of core diagrams running west to east, with SB105 to the west near the mouth of Yosemite Creek, SB79 to the east in front of the former landfill, and the other cores in between. The core sections plot depth on the left and percent EM composition on the bottom, with each EM color coded to the EM bar-graphs at the top of the figure. The gray sections on the left of each core show the sampled horizons in each core, where ACF measurements are present (distributions are interpolated in core sections where no ACF data are available). From this presentation it appears that surface samples in SB79 located in the east by the landfill are mainly green indicating a high contribution of EM2 (Aroclor 1260). Samples from core SB106 located in the west by Yosemite Creek are mostly blue, indicating higher EM3 compositions (Aroclor 1260 with secondary amounts of lower chlorinated congeners). Samples between SB-105 and SB-79 show a mix with more blue (EM3) to the west and more green (EM2) to the east. In most of the cores, the percent of Aroclor 1254 (red) increases as a function of depth. It is interesting to note that Pb210 dating done at core SB94 shows a major change in composition at 30 cm which is around 1968 (with a sedimentation rate of 0.9 cm/year and cores collected in 2001 [Battelle, 2007]).

6.6.2 Ashtabula Case Study

At the Ashtabula River dredge site there are four EMs, although one pattern appears to be dechlorination so it likely represents the dominant Aroclor 1248 source that has undergone post-release alteration. Figure 8 shows the EM compositions for a PVA model run for four EMs (see Section 5.5 in the Final Report for details of the PVA model for four EMs). Note also that for the Ashtabula model there were 83 congeners versus the 38 congeners for HPS. The additional congeners at the Ashtabula site allow us to better discriminate alteration (dechlorination) from original source patterns. If we had only analyzed the 38 congeners used for the HPS site, we would not have seen the major dechlorination pattern from PCB25 and PCB26 since these congeners were not run at HPS. Core diagrams for selected Ashtabula River data are shown in Figure 9, which represents a transect of cores from upstream on the left to downstream on the right. These cores were chosen to show the general relationships between EMs in the dredge area, but multiple other transects could be constructed from other cores at the site. Core diagrams are plotted in elevation above sea level on the left, and percent EM composition along the bottom color coded to EMs from Figure 8. Numbers to the right of each core horizon are total PCB concentrations in ppm (i.e., mg/kg). The most obvious feature of these core diagrams is that most of the cores show >90% have a source of Aroclor 1248 (including some with dechlorination). Deeper sections of the cores show increasing amounts of the heavier “Deca” source, but the majority is still Aroclor 1248. There are only sporadic indications of the

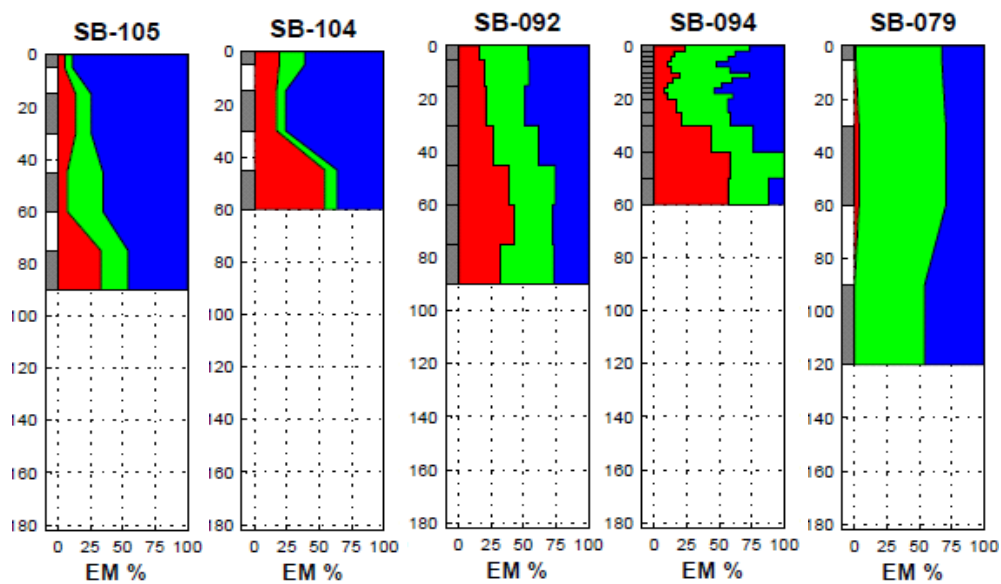
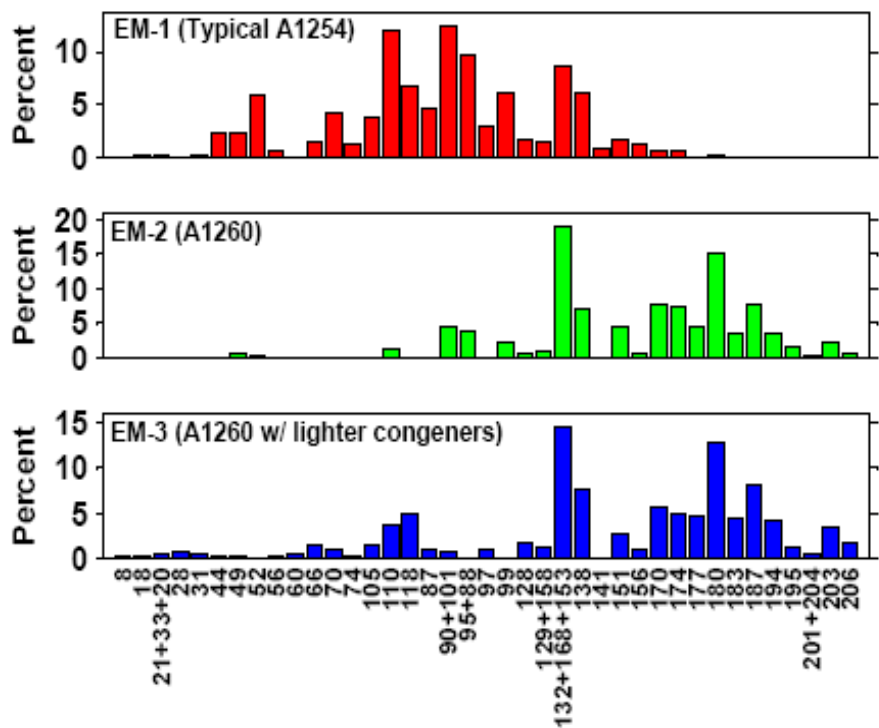


Figure 7. HPS EM source compositions and EM percent in selected cores.

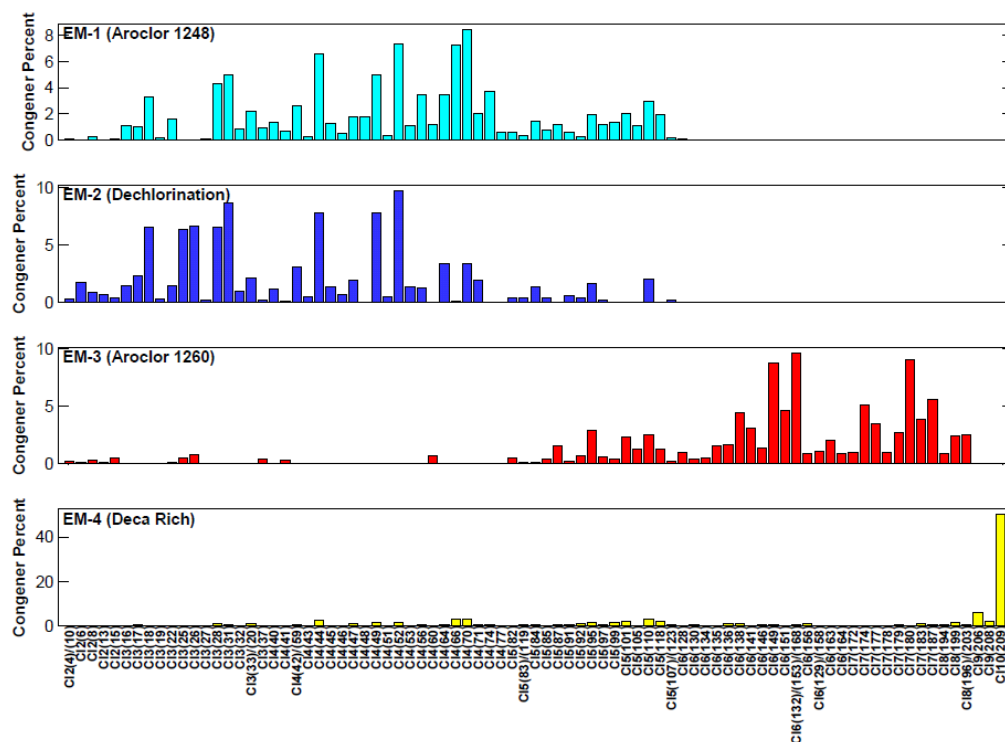


Figure 8. Ashtabula EM compositions.

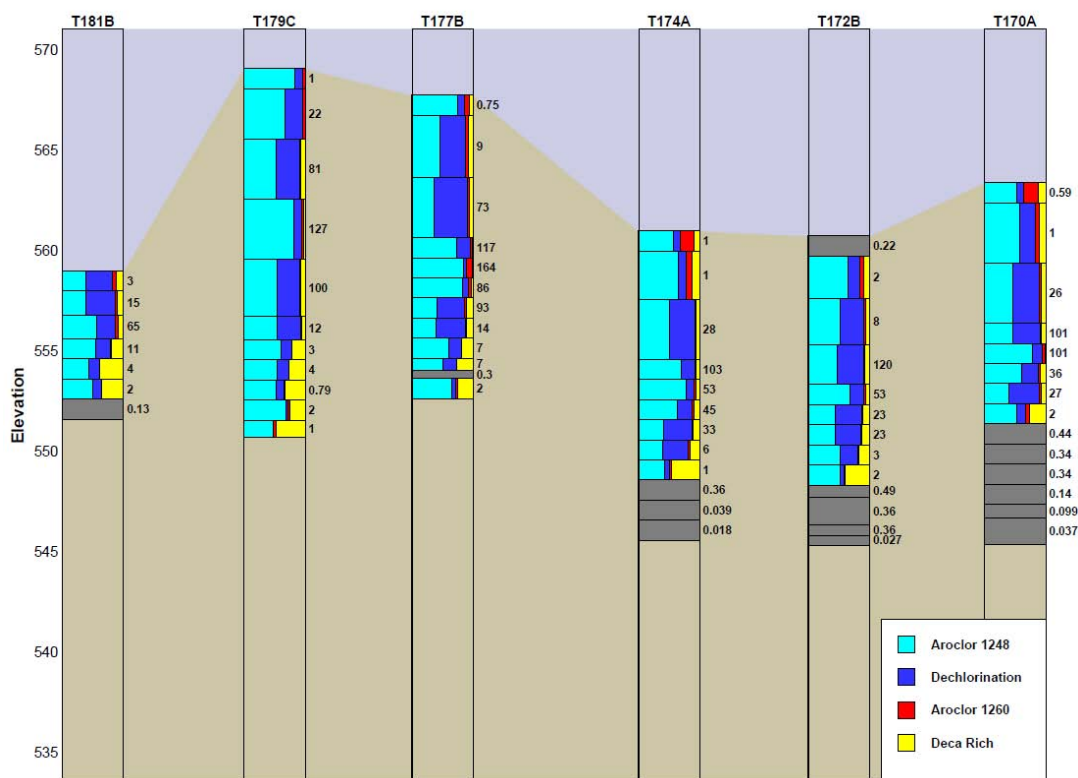


Figure 9. Selected Ashtabula cores showing EM percent compositions and total PCB levels (ppm).

6.6.3 Source Confirmation

At HPS we have additional onshore studies (Battelle, 2007) that confirm the beach in front of the landfill is a current source of Aroclor 1260 (EM2) to the nearshore sediments, but lack confirmation of the Yosemite Creek outfall PCB pattern that might match the EM3 pattern that occurs in more recent sediments in the Yosemite Creek area. At the Ashtabula River dredge site the probable sources of the Aroclor 1248 (and dechlorinated Aroclor 1248) and Deca-rich patterns are likely from Fields Brook, although actual source patterns from Fields Brook were not collected so we base this conclusion on previous reported work (EPA, 1998; Imamoglu et al., 2002; Battelle, 2010). The more recent Aroclor 1260 pattern from drainage near Jacks Marine was identified during preliminary work done for the EPA dredge project (Battelle, 2010) so they could ensure all continuing sources had been contained before proceeding with the dredge project. At both of our demonstration sites, the use of existing study designs and samples allowed for a more cost-effective forensics demonstration but also resulted in similar limitations. Without additional analysis of upstream source areas, positive confirmation of the actual PCB sources to our two demonstration site areas is still incomplete. Although this additional confirmation work is outside the scope of this ESTCP project, if this were an actual forensics project this additional confirmation work might be conducted to provide more conclusive evidence of the actual upstream PCB sources. For future forensics studies it might be best to plan to collect these upland/upstream samples for analysis to confirm sources. The best way to accomplish this might be an iterative approach where additional ACF samples are run from locations near the suspected source areas to better define the EM source compositions. This iterative approach could also be used to run some additional samples from upland/upstream of these same source areas in an attempt to match the actual sources. At HPS this was done with upland samples from the landfill shoreline area for the source of EM2 (but this shoreline source material was only present as a source after this section of shoreline was filled in the 1960-1970 time period). Additional work might also include going to upstream Yosemite Creek CSOs and collecting upstream sump material which might require opening manhole covers upland from the outfalls opening to the bay. For Ashtabula sources, additional source samples may need to be collected upstream in Fields Brook and the drainage across the river near Jacks Marine. Additional guidance on actually performing a fingerprinting study at a site can be found in this report's references and a companion user's guide on the Navy's SPAWAR website (http://environ.spawar.navy.mil/Projects/PCB_Fingerprinting).

7.0 PERFORMANCE ASSESSMENT

As stated in Table 1 and Section 3, the performance objectives have certain data requirements and success criteria that need to be met. This section describes how these data were used to evaluate the demonstration and show how the performance objectives for a successful demonstration have been met.

7.1 PERFORMANCE OBJECTIVE 1: PARCC PARAMETERS FOR RSC/ACF

Both the RSC and ACF measurements are modifications of standard EPA methods, and both can be evaluated by similar data quality objectives employed by EPA laboratories. This includes the evaluation of data quality parameters that can be characterized by five indicators of data quality referred to as the PARCC parameters: precision, accuracy, representativeness, completeness, and comparability. The specific types of quality assurance (QA) samples that can be used to evaluate precision and accuracy vary, with additional measures for the other PARCC parameters.

7.1.1 RSC Quality Control Results

The more detailed results in Section 6.1 of the Final Report show the RSC data pass DQO tests for the PARCC parameters. These RSC data therefore represent high quality data that pass all our tests for data quality and are ready for use in a forensics study.

7.1.2 ACF Quality Control Results

The more detailed results in Section 6.1 of the Final Report show the ACF data pass DQO tests for the PARCC parameters. These ACF data therefore represent high quality data that pass all our tests for data quality and are ready for use in a forensics study.

7.2 PERFORMANCE OBJECTIVE 2: DATA ANALYSIS TECHNIQUES

Multiple levels of graphical and statistical analyses are possible to investigate the forensics data. Section 6.2 in the Final Report contains details of the method comparisons used to compare the various receptor models commonly used in forensic studies. In evaluating the results of these methods, note that Figure 10 shows all four resolved very similar congener patterns for the proposed EM sources at HPS. Note also that two of the three patterns are highly collinear (that is two patterns have a high similarity to Aroclor 1260). Figure 11 shows the spatial relationships for these HPS EM sources in the surface sediments. The mixing proportions for these four different methods show a high degree of similarity. The take home message of this receptor model method comparison is that all four methods provide similar results. But when faced with bad data, any or all of these methods can produce spurious results. One of the most crucial steps in the data analysis process is vigilant outlier detection and data cleaning. Even with good data, these methods can be problematic in the hands of an inexperienced user and/or a user without sensitivity to PCB chemistry and familiarity with the specific site and its contaminant history. In the hands of an experienced practitioner, these methods should result in source patterns and contributions that are consistent.

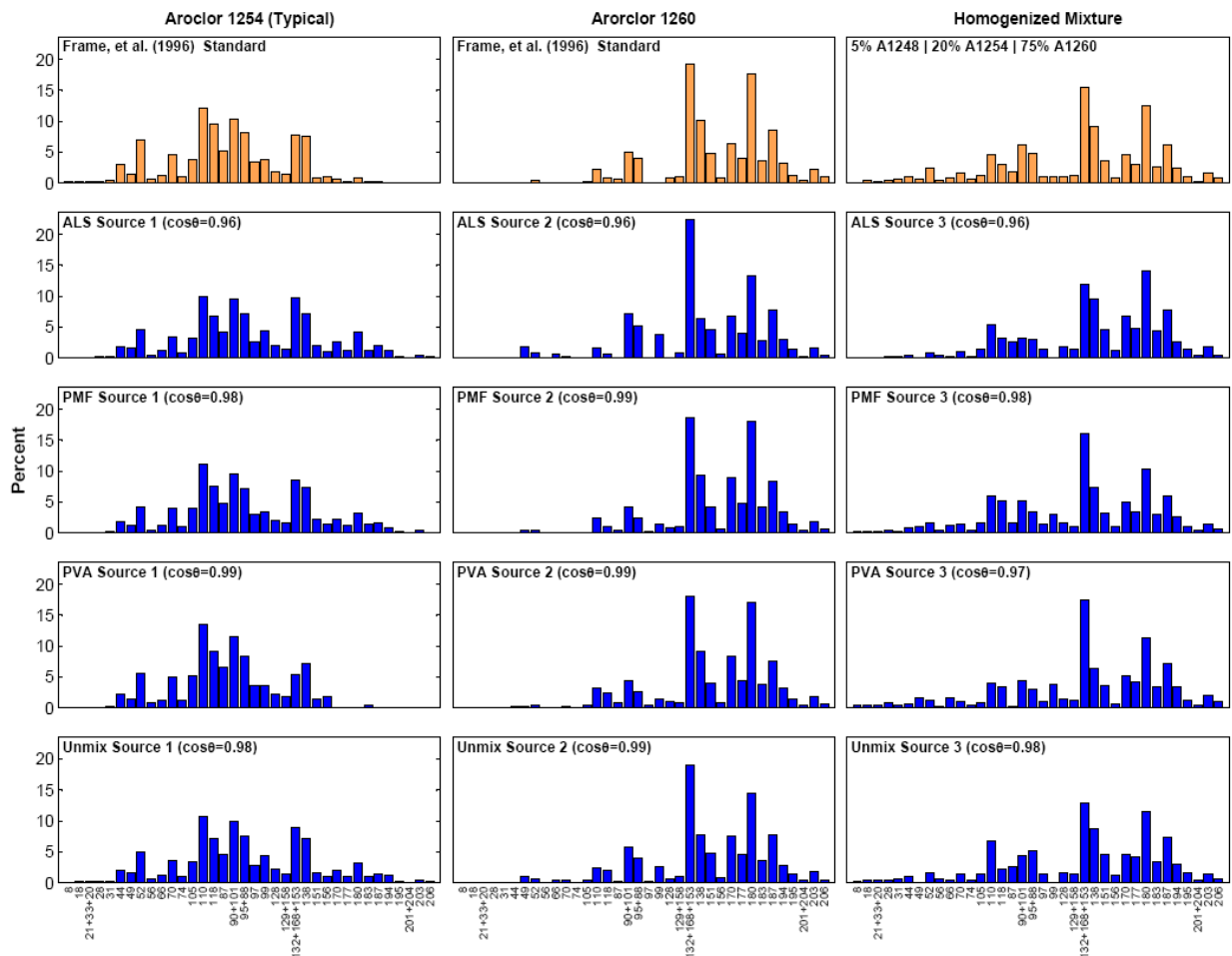


Figure 10. Comparison of source compositions derived from ALS (row 2), PMF (row 3), PVA (row 4), and Unmix (row 5).
 Cos θ value at the top of each bar graph indicates the similarity of each profile to the interpreted source profile (row 1), as calculated with the cosine theta similarity metric with 1.00 indicating perfect fit.

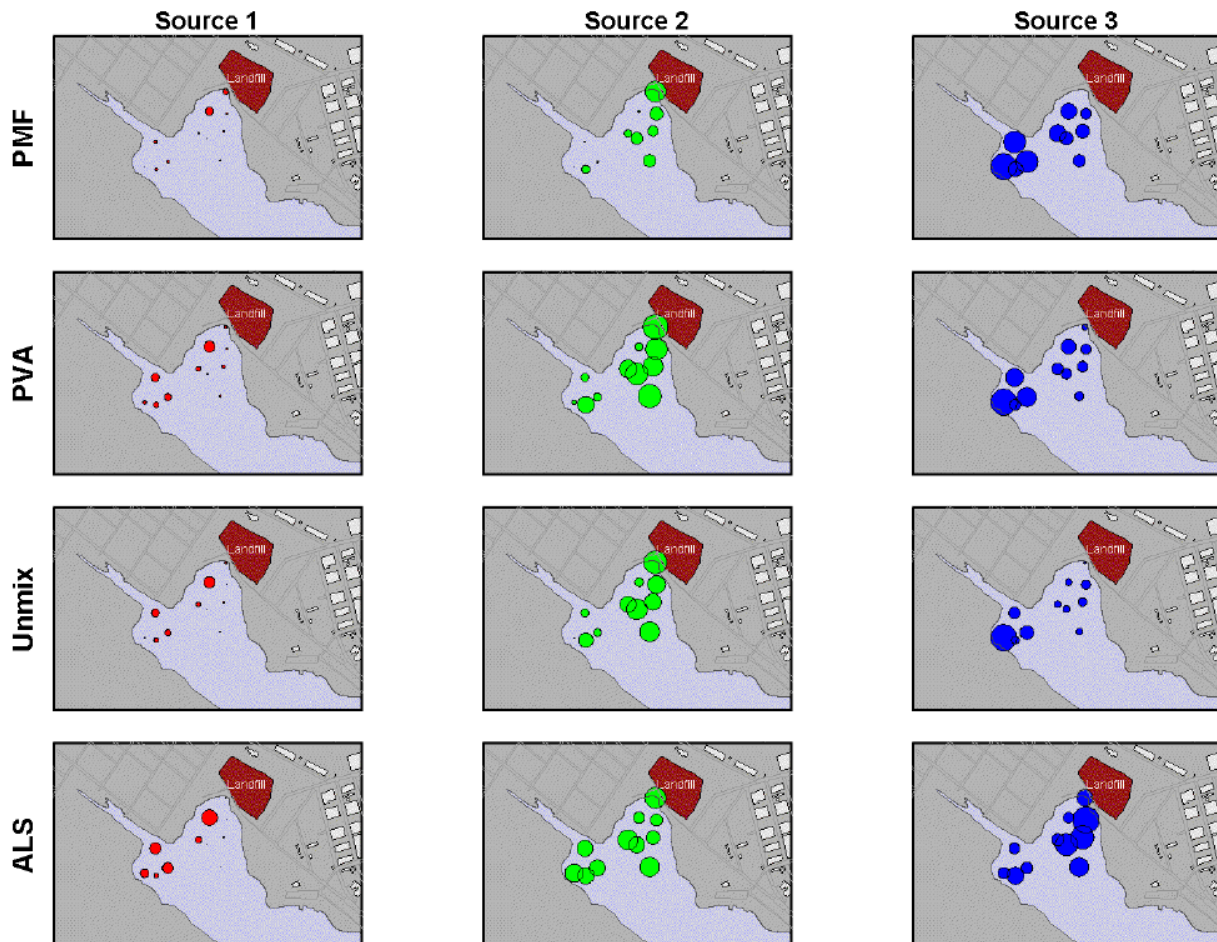


Figure 11. Comparison of source apportionment derived from PMF, PVA, Unmix, and ALS for surface sediments.

Bubble size is proportional to percent contribution in surface sediments. Source 3 appears more common by Yosemite Creek, Source 2 is more common by former landfill, and Source 1 is usually more common at depth in all areas but shown here in these surface plots.

The overall conclusion of this method comparison is that these receptor model methods have passed their performance evaluation. Given a dataset that has undergone some measure of preparation to overcome problems associated with non-detects, interferences, and other analytical errors, all of these receptor models should produce a similar apportionment of PCB sources during a forensics study. The greatest concern is therefore that the PCB dataset should be of high quality, so that any required preparation will be minimal. And of course the receptor models require a certain level of expertise, but given these prerequisites these receptor models can perform a successful forensics study. Given either a simple artificial dataset or a more realistic “real” dataset, these techniques have passed the above tests for accuracy and precision as part of their performance assessment detailed more fully in the Final Report.

This page left blank intentionally.

8.0 COST ASSESSMENT

ESTCP projects are required to develop and validate, to the extent possible, the expected operational costs of the technology. By incorporating pre-existing data into the study, it was possible to leverage the costs of this ESTCP project with the earlier HPS assessment and EPA Ashtabula River dredge projects. This provided significant cost savings to this ESTCP project, especially with analytical costs and field deployment costs. Ideally, a potential forensic investigation can be incorporated into the larger site investigation, and data obtained from both can be used for forensic interpretation as well as meet other project needs. Although this is not always possible, any such coordinated sample collection and analysis can significantly reduce costs since sampling and analysis is often the most expensive part of a study.

8.1 COST ANALYSIS

It is very difficult to place a cost estimate for a forensics study since there are so many site specific variables. The costs in Table 2 are based on the collection of 100 surface sediment samples, which are analyzed by RSC. A total of 25 of the 100 samples would subsequently also be analyzed by ACF methods, with collection costs assumed to be covered by RSC. These analytical costs for the ACF analysis in Table 2 assumes that the analysis is conducted for the analysis of 100+ PCB congeners using GC/low-resolution MS with the spectrometer operating in selected ion monitoring mode (GC/LRMS-SIM). This is the optimal analytical approach for most PCB sediment analysis. However, GC/HRMS (e.g., EPA Method 1668a) does provide even better sensitivity and selectivity, but the additional cost (approximately 50-100% higher analytical cost) can rarely be justified for a sediment PCB investigation, unless the data are also to be used for human health risk assessment purposes (Method 1668a can generate more reliable data for a small set of PCB congeners that are particularly important for risk assessment, such as PCB77, PCB81, and PCB126). The need for sediment coring (i.e., to gain historical data) would increase the sample collection and, most likely, the analytical costs as it would typically result in more samples in addition to more complicated sample collection.

As discussed earlier, the costs in Table 2 reflect a stand-alone forensic investigation, for a total cost of approximately \$184,000. This cost estimate is for a relatively straight forward investigation, with no need for comprehensive characterization (e.g., collection of sediment cores). Forensic investigations are often conducted at sites that are already being investigated (e.g., as part of an RI/FS investigation) and a forensic investigation can then cost effectively be included in the overall scope. Many of the cost elements in Table 2 would be part of most environmental site investigations, and the incremental cost to modify the scope of the investigation and also conduct a forensic study is notably less, as indicated at the bottom of Table 2. Adding a forensic component could possibly cost just about half of conducting a dedicated forensic investigation, but this will depend on the amount of overlap with the other regulatory program. Some additional costs for an added forensic component to a regulatory project might include additional costs to run a greater number of congeners (100 versus 22), which is not included here. The best cost savings measure is to plan carefully and conduct a forensics study along with other regulatory projects similar to what was done for this ESTCP project. That is the most cost-effective strategy for conducting a forensics project at most DoD sites.

Table 2. Approximate costs for a contaminated sediment forensics study.

Cost Element	Approximate Cost	Comment
Step 1: Site selection	N/A	The decision to investigate a site is generally made outside the site project and budget.
Step 2: CSM (Baseline characterization)	\$20,000	Compilation of pre-existing data, reports, and site history. Develop hypotheses of possible sources of contamination. Cost can vary significantly based on the availability of historical data and information, and the complexity of the site.
Step 3: Study design	\$30,000	Develop the study plan, including work plan and sampling and analysis plan, describing the key elements of conducting the forensic study.
Step 4: RSC		
Field deployment/sampling	\$40,000	Deployment of field team and sample collection.
Sample analysis	\$12,000	Sample PCB analysis.
Data compilation/analysis	\$4,000	Compilation and preliminary summary and analysis of the data.
Step 5: ACF		
Field deployment/sampling	Covered in Step 4	Deployment of field team and sample collection, if needed for ACF samples. Sample PCB analysis. Compilation and preliminary summary and analysis of the data.
Sample analysis	\$16,000	
Data compilation/analysis	\$12,000	
Step 6: Final report	\$50,000	Data analysis, interpretation, and report preparation.
Total cost for a stand-alone forensic study		\$184,000
Total incremental cost to add a forensic study to a site investigation ^a		\$91,000 ^a

^aThe field deployment/sampling and sample analysis costs for RSC and ACF are not typically needed if the forensic investigation can be well coordinated with other site investigations. The costs associated with developing the CSM and Study Design may also be reduced if such can be coordinated with other site investigations, so here are reduced by half.

Unlike most other ESTCP projects, this project does not lend itself to comparing to alternative technologies to perform a cost comparison. The alternative is to not conduct a forensic investigation, which would result in incomplete and possibly erroneous understanding of sources. So rather than looking for cost savings compared to an alternative technology, it is more appropriate to look at potential cost avoidance in using forensic studies. With a technically-defensible apportionment method such as the one described in this report, it may be possible to share the remediation costs with other PRPs. Additional cost avoidance may also be realized if all sources of contamination are identified up front and contained prior to any remedial efforts, so no continuing sources of contamination force repeated rounds of remedial efforts at additional cost to clean the sediments.

9.0 IMPLEMENTATION ISSUES

As discussed in several previous sections of this report, a forensics study requires high-quality data and an experienced team. A geochemist is required to ensure the data quality is sufficient to conduct any of the described statistical analyses. A statistical analyst must be experienced with the particular techniques such as the receptor models used to determine source information. And the project manager needs to interpret all these data and integrate them into the regulatory program so they will prove useful to making regulatory decisions. If the regulatory project is not prepared to use the forensic results, then any forensics project may turn out to be a waste of time and effort. It therefore becomes important to assess the regulatory program under which the site operates to determine how receptive they will be to the forensic study results. To avoid litigation among the various PRPs, some type of arbitration is often employed. It is therefore important to have a technically-defensible approach (such as the one described in this report) that can be presented to an impartial arbitrator so that the DoD's case is fairly represented. Many PRPs will often bring their own experts and their receptor models for arbitration, so the DoD should have access to the best technical arguments for apportionment among PRPs. Often a final decision from arbitration will be some negotiated solution that represents some compromise between the positions argued by the various PRPs. In that case it is important to have the best, most technically-defensible forensics study that is possible.

All of the techniques discussed in this report are commercially available from multiple sources. The analytical techniques are available from contractors that can provide high quality data. Detection limits for individual PCB congeners for ACF data in this report were around 0.1 ppb (i.e., $\mu\text{g/kg}$), so that samples with total PCB concentrations above 100 ppb provided a dataset of 38 congeners at the first demonstration site (for HPS) and total concentrations above about 500 ppb provided a dataset of 83 congeners at the second demonstration site (for Ashtabula). The number of individual congeners that can be expected to be above detection limits will be related to the total concentration of the samples, and samples with total PCB concentrations below about 100 ppb will not have enough congeners above detection limits to be useful for forensic study. This 100 ppb limit is also the detection limit (assuming no matrix interferences which may raise detection limits) of the RSC immunoassay used at HPS. The data analysis and interpretation techniques are also widely available, with some (Unmix and PMF) available free of charge to download from EPA websites. Just as we would recommend spending a little more money to obtain a contract laboratory that can provide higher quality data with lower PCB congener detection limits, we would also recommend paying extra to find a contractor with data analysis experience in the type of forensic study that you wish to conduct rather than downloading fingerprinting techniques yourself from the internet. These contractors should also have experience with many types of visual displays that can be used to present the data in a comprehensible fashion. Additional guidance on conducting PCB fingerprinting studies can be found in a companion user's guide on the Navy's SPAWAR website (http://environ.spawar.navy.mil/Projects/PCB_Fingerprinting).

This page left blank intentionally.

10.0 REFERENCES

- Battelle and SEA Engineering, 2010. Field Study on Environmental Residuals: Ashtabula River. Volume I, Final Report. EPA Contract No. EP-C-05-057 Task Order 50. Submitted to U.S. EPA NRMRL-ORD. September, 2010.
<http://www.epa.gov/nrmrl/pubs/600r10126/600r10126.pdf>
- Battelle, Neptune and Co, and SEA Engineering, 2007. Technical Memorandum Hunters Point Shipyard Parcel F Feasibility Study Data Gaps Investigation San Francisco Bay, California. U.S. Navy Contract No. N68711-01-F-6102. Submitted to U.S. Navy-BRAC, San Diego, CA. May 25, 2007.
- Barabas, N., P. Goovaerts, and P. Adriaens, 2004. Modified polytopic vector analysis to identify and quantify a dioxin dechlorination signature in sediments. 2. Application to the Passaic River. *Environ. Sci. Technol.* 38, 1821-1827.
- Bzdusek, P.A., E.R. Christensen, C.M. Lee, U. Pakdeesusuk, and D.L. Freedman, 2006. PCB Congeners and Dechlorination in Sediments of Lake Hartwell, South Carolina, Determined from Cores Collected in 1987 and 1998. *Environ. Sci. Technol.* 40:109-119.
- Durell, G.S., V. Magar, and R. Brenner, 2001. Natural Dechlorination and Detoxification of PCBs in a Contaminated Sediment Environment. International Conference on Remediation of Contaminated Sediments, Venice, Italy, October 10-12, 2001.
- Durell, G.S., and J. Seavey Fredriksson, 2000. PCB Congener and PCB Homologue Analysis by HRGC/LRMS; A Low MDL, Cost Effective Analytical Alternative for Tomorrow's Quality Sensitive PCB Assessments. 23rd EPA Conference on Analysis of Pollutants in the Environment, Pittsburgh, PA, May 14-16, 2000.
- Emsbo-Mattingly, S., and G. Durell, 2003. Identifying PCB Mixtures and Compositional Changes in Sediments with Low-resolution Mass Spectrometry and Environmental Forensic Interpretation Tools. Seventh International In Situ and On-site Bioremediation Symposium, Orlando, Florida, June 2-5, 2003.
- Gilbert, R. O., 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York, NY.
- Hopke, P.K., K. Ito, T. Mar, W.F. Christensen, D.J. Eatough, R.C. Henry, E. Kim, F. Laden, R. Lall, T.V. Larson, H. Liu, L. Neas, J. Pinto, M. Stolzel, H. Suh, P. Paatero, and G.D. Thurston, 2006. PM source apportionment and health effects: 1. Intercomparison of source apportionment results. *J Expo Sci Environ Epidemiol.* 2006 May;16(3):275-86.
- Imamoglu, I., K. Li, and E.R. Christensen, 2002. Modeling Polychlorinated Biphenyl Congener Patterns and Dechlorination in Dated Sediment from the Ashtabula River, Ohio, USA. *Environ. Tox. Chem.*, 21(11):2283-2291.

- Jarman, W.M., G.W. Johnson, C.E. Bacon, J.A. Davis, R.W. Risebrough, and R. Ramer, 1997. Levels and patterns of polychlorinated biphenyls in water collected from the San Francisco Bay and Estuary, 1993-1995. *Fresenius J. Anal. Chem.* 359: 254-260.
- Johnson, G.W., W.M. Jarman, C.E. Bacon, J.A. Davis, R. Ehrlich, and R.W. Risebrough, 2000. Resolving polychlorinated biphenyl source fingerprints in suspended particulate matter of San Francisco Bay. *Environ. Sci. Technol.* 34:552-559.
- Johnson, G.W., J.F. Quensen, III, J. Chiarenzelli, and C. Hamilton, 2006. Chapter 10: Polychlorinated Biphenyls. In: *Environmental Forensics: A Contaminant Specific Guide* (R. Morrison and B. Murphy, eds.). Elsevier. Amsterdam. pp. 187-225.
- Johnson, G.W., R. Ehrlich, W. Full, and S. Ramos, 2007. Chapter 6: Principal components analysis and receptor models in environmental forensics. In: *An Introduction to Environmental Forensics*. 2nd Edition. (R. Morrison and B. Murphy, eds.). Elsevier. Amsterdam. pp. 207-272.
- Magar, V.S., G.W. Johnson, R.C. Brenner, J.F. Quensen, E.A. Foote, G. Durell, J.A. Ickes, and C. Peven-McCarthy, 2005. Long-term recovery of PCB-contaminated sediments at the Lake Hartwell superfund site: PCB dechlorination. 1. End-member characterization. *Environ Sci Technol.* 39(10):3538-47.
- Rodenburg, L.A., S. Du, D.E. Fennell, and G.J. Cavallo, 2010. Evidence for Widespread Dechlorination of Polychlorinated Biphenyls in Groundwater, Landfills, and Wastewater Collection Systems. *Environ. Sci. Technol.* 44:7534-7540.
- Stout, S.A., J.M. Leather, and W.E. Corl, 2003. A User's Guide for Determining the Sources of Contaminants in Sediment: A Demonstration Study of PAH Sources in Sediments in the Vicinity of the Norfolk Naval Shipyard, Elizabeth River, Norfolk Virginia. SPAWAR Technical Report 1907, 97pg.
<http://www.spawar.navy.mil/sti/publications/pubs/tr/1907/tr1907cond.pdf>
- U.S. Environmental Protection Agency (EPA), 1998. Project Update Fields Brook Superfund Site. Office of Public Affairs, Region 5 Fact Sheets.
http://www.epa.gov/region5/cleanup/fieldsbrook/pdfs/fieldsbrook_fs_199811.pdf
- EPA, 2002. Draft "Contaminated Sediment Remediation Guidance for Hazardous Waste Sites". OSWER 9355.0-85 Draft.
<http://www.epa.gov/superfund/resources/sediment/documents.htm>

APPENDIX A

POINTS OF CONTACT

Point of Contact	Organization	Phone Fax E-Mail	Role In Project
Jim Leather	Navy SPAWAR	Phone: (619) 553-6240 E-Mail: jim.leather@navy.mil	Overall Program Manager
Greg Durell	Battelle	Phone: (781) 952-5233 E-Mail: durell@battelle.org	Lead on ACF
Glenn Johnson	University of Utah	Phone: (801) 581-6151 E-Mail: gjohnson@egi.utah.edu	Lead on Statistical Methods
Marc Mills	EPA	Phone: (513) 569-7322 E-Mail: mills.marc@epamail.epa.gov	EPA Coordinator
Andrea Leeson	ESTCP 4800 Mark Center Drive Suite 17008 Alexandria, VA 22350-3605	Phone: (571) 372-6398 E-Mail: andrea.leeson@osd.mil	Environmental Restoration Program Manager



ESTCP Office

4800 Mark Center Drive
Suite 17D08
Alexandria, VA 22350-3605
(571) 372-6565 (Phone)
E-mail: estcp@estcp.org
www.serdp-estcp.org